# PHENOLS OF THE ESSENTIAL OIL OF Abies sibirica

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Fir essential oil is widely used as a raw material for the production of synthetic camphor, and its medical properties have long been known. This explains the interest in the composition of all the components of fir oil. There is very little information on the phenols of the essential oils of conifers, and it is known only [1] that o-, m-, and p-cresols have been found in the essential oil of Pinus silvestris growing in Finland.

We have investigated the phenols isolated from the essential oil of Abies sibirica Ldb. growing in Krasnoyrask territory. The essential oil was obtained in the Poima lespromkhoz [forestry farm]. The phenols were extracted from the essential oil by a standard method [2], their yield being 0.15% on the oil. The composition of the phenols was determined by the GLC method on a LKhM-72 chromatograph with a thermal conductivity detector. Analysis was performed on a 3000 × 4 mm column with Apiezon L as stationary liquid phase, deposited in an amount of 15% on Chromosorb W with a grain size of 0.250-0.315 mm. The column was heated with programming of the temperature from 85°C to 340°C at the rate of 2.5°C/min. The temperature of the detector was 250°C and that of the evaporator 285°C, and the rate of flow of carrier gas (helium) was 75 ml/min.

All the phenols were identified by additions of the pure substances. The relative retention times and the quantitative composition of the phenols, calculated by the method of internal normalization with respect to the areas of the peaks, are given below:

| Phenol | Relative retention time | Amount, % |
|---|---|---|
| Phenol | 0,48 | 0,30 |
| $X_1$ | 0,55 | 1,04 |
| o-Cresol | 0,58 | 1,54 |
| m-Cresol | 0,59 | 5,73 |
| p-Cresol | 0,64 | 1,91 |
| Guaiacol | 0,68 | 1,08 |
| $X_2$ | 0,70 | 0,52 |
| 2,4-Dimethylphenol | 0,73 | 1.18 |
| 2,6-Dimethylphenol | 0,75 | 5,87 |
| 2,5-Dimethylphenol + ethylphenol | 0,82 | 3,36 |
| 3,5-Dimethylphenol | 0,86 | 8,90 |
| 2,3-Dimethylphenol | 0,89 | 7,84 |
| $X_3$ | 0,90 | 8,71 |
| Pyrocatechol | 0,93 | 8,72 |
| Hydroquinone | 1,00 | 1,67 |
| tert-Butylphenol | 1,05 | 4.11 |
| 2,4,6-Trimethylphenol | 1,10 | 9,31 |
| Resorcinol | 1,13 | 5,64 |
| 2-Methylresorcinol | 1,17 | 9,85 |
| 3,4,5-Trimethylphenol | 1,19 | Traces |
| p-n-Butylphenol | 1,23 | 1,99 |
| $X_4$ | 1,27 | 3,10 |
| Dimethylresorcinol | 1,31 | 2,37 |
| $X_5$ | 1,33 | 2,00 |
| Ethylresorcinol | 1,38 | 1,05 |
| $X_6$ | 1,45 | 0,24 |
| β-Naphthol | 1,48 | 0,16 |
| $X_7$ | 1,52 | 0,20 |
| α-Naphthol | 1,57 | 0,39 |
| Pentamethylphenol | 1,63 | 0,17 |

The results of the investigation showed that the composition of the phenols of the essential oil of Abies sibirica is extremely complex. The number of phenols detected was 32, among which the main components are 3,5-dimethylphenol, 2,3-dimethylphenol, pyrocatechol, 2,4,6-trimethylphenol, 2-methylresorcinol, and the unidentified compound $X_5$.

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# METHOD FOR THE QUANTITATIVE DETERMINATION OF CNICIN IN Centaurea squarrosa

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The sesquiterpene lactone cnicin has been isolated from the epigeal part of Centaurea squarrosa (family Compositae) [1].

In the present paper we propose a method for the quantitative determination of cnicin consisting in the extraction of the combined lactones from the plant raw material by the method described [1], its chromatographic separation, and the determination of the lactone in the eluate by a micromethod of volumetric analysis. The completeness of extraction was checked chromatographically on "Silufol" plates in the solvent system chloroform–ethanol (9:1). The cnicin was separated from the accompanying substances in a thin fixed layer of silica gel in the same system. On elution with chloroform–ethanol (9:1) 97-99% desorption was achieved. The amount cnicin in the eluate was determined by an acidimetric method after saponification of the lactone with alkali.

The optimum conditions (concentration of alkali, solvent, time of hydrolysis) in which, in addition to the opening of the lactone ring, hydrolysis of the ester group of cnicin takes place were determined by special experiments. Then a gram-equivalent of cnicin will be equal to half a gram-molecule. Below we give the results of a statistical treatment of the determination of microamounts of cnicin (0.5-2.0 mg):

| $n$ | $\overline{x}$ | $S^2$ | $S$ | $S_{\overline{x}}$ | $a$ | $t_{a,k}$ | $\varepsilon_a$ | $E_{\text{rel}}$ |
|---|---|---|---|---|---|---|---|---|
| 5 | 97,0% | 0,598 | 0,773 | 0,334 | 0.95 | 2,776 | 0,955 | 0,98% |

The amount of cnicin in the raw material was found in the following way: 10 g (weighed with an accuracy of 0.01 g) of the comminuted air-dry raw material was exhaustively extracted with 95% ethanol, and the extract was evaporated to give the total lactones [1], which were dissolved in 20 ml of ethanol. On a plate (13 × 18 cm) with a fixed layer of silica gel (type KSK, particle size 0.16-0.10 mm; pH of a 10% aqueous solution 8.2), 0.3 ml of the ethanolic solution was deposited and chromatography was carried out in the system given above. On the same plates was placed a "marker" – 0.05 ml of a 0.25% ethanolic solution of cnicin, which was revealed with a 1% solution of vanillin in concentrated sulfuric acid (Rf 0.40). The lactone was eluted with 50 ml of the mixture mentioned in a Schott No. 4 funnel, the eluate was evaporated to dryness, the residue was dissolved in 1 ml of ethanol, and 2 ml of 0.01 N caustic soda solution was added and saponification was performed for 5 min. The excess of alkali was back-titrated in the hot state [2] with a 0.01 N solution of hydrochloric acid until the blue color of the solution had disappeared (indicator: thymolphthalein).

The amount of cnicin in the raw material (x, %) on the absolutely dry weight was calculated from the formula

$$x = \frac{10 \cdot \left( V_1 - \frac{N_{\text{acid}} \cdot V_{\text{acid}}}{N_{\text{alk}}} \right) N_{\text{alk}} \text{E} \cdot V_2}{p \cdot V_3 (100 - h)},$$

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